

Hydrothermal systems and mineralization of volcanic arcs: Comparison of West Pacific and Mediterranean arcs

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Introduction

Hydrothermal systems and their associated metal deposits have been studied at oceanic spreading centers since the late 1970s when they were first discovered. More recently, those studies have been extended to subduction zone hydrothermal systems including active volcanic arcs and back-arc environments. Oceanic spreading centers compose a global ridge system where new ocean crust is formed (divergent boundary) and extends for about 64,000 kilometres (km). Volcanic arc hydrothermal systems form where ocean crust is consumed by subduction (convergent boundary) which creates a chain of volcanoes, both submarine and subaerial, and back-arc spreading in some arc systems (Fig. 1); these two together add another 25,000 km to the zone of global volcanism and hydrothermal activity. Back-arc basins generally form via seafloor spreading, similar to that at oceanic ridges.

Recent studies have concentrated on hydrothermal systems in West Pacific and Mediterranean Sea volcanic arc and back-arc basin subduction systems and associated mineral deposits, which range from high-temperature sulphide-sulphate deposits, low- to intermediate temperature sulfur and silica deposits, and low-temperature iron-oxide and manganese-oxide deposits (e.g., Alfieris et al., 2013; Dando et al., 1999; Hein et al., 2000, 2008, 2013; Kilias et al., 2001; Petersen et al., 2013). Here we provide a brief background on hydrothermal systems and then compare Pacific and Mediterranean hydrothermal volcanic arc deposits.

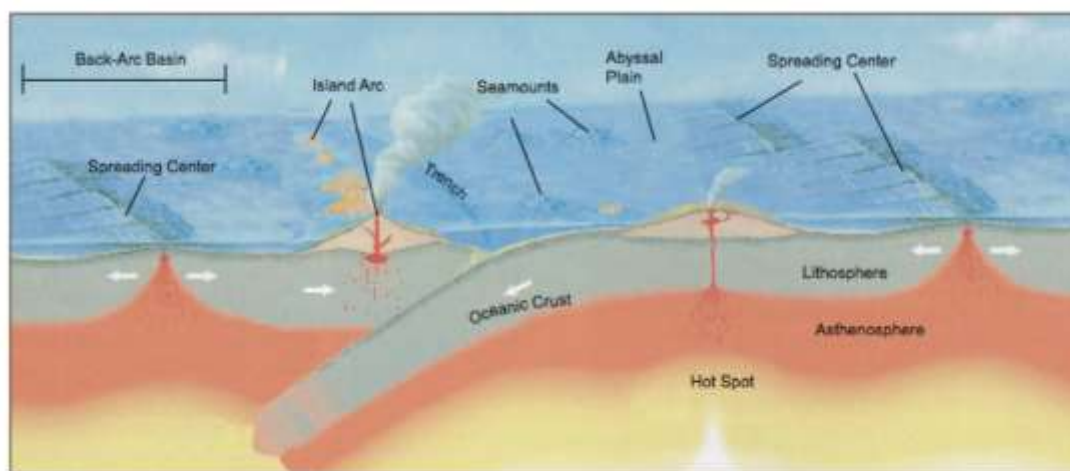


Figure 1: Cross-section of spreading center, subduction zone, and back-arc spreading, all of which are locations of precipitation of hydrothermal metal deposits (modified from Vigil and Tilling, 2006).

Hydrothermal circulation and controls on deposit composition

Most hydrothermal systems undergo a similar sequence of development. In areas of volcanic activity, fractures in the seafloor allow seawater to penetrate several kilometres depth where it approaches a magmatic heat source (Fig. 2). The seawater heats up to as high as about 400° C, and becomes acidic, reduced, and chemically reacts with the surrounding rocks leaching metals and other elements. The fluid becomes enriched in dissolved metals and sulphur. As it heats up, the fluid loses density and rises to the seafloor where it encounters cold seawater. Because of the change in temperature, redox state, and pH, the dissolved metals precipitate as minerals at the seabed in the form of chimneys and mounds, below the seabed as stratabound deposits and vein systems, and as fallout from a hydrothermal plume. The descending seawater and rising hydrothermal fluid form a hydrothermal circulation cell (Fig. 2). The rising fluid can lose heat by conductive cooling, which can influence the suite of minerals that is produced. The mineral assemblages formed in these focused-flow hydrothermal systems can vary widely from place to place, with the most common mineral being the iron sulphide pyrite, and the minerals of economic interest chalcopyrite (copper sulphide), sphalerite (zinc sulphide), and galena (lead sulphide); the most common sulphates are anhydrite, gypsum, and barite. X-ray amorphous silica is also very common. Gold and silver are usually associated with one or more of the sulphide minerals or occur as sulphosalts. Bismuth, cadmium, gallium, germanium, antimony, tellurium, thallium, and indium also occur in these focus-flow hydrothermal deposits and can be in concentrations of economic interest in some deposits, especially those that occur in volcanic arc settings.

If the rising fluid loses heat by mixing with descending seawater, then diffuse-flow hydrothermal systems develop (Fig. 2). Diffuse-flow systems commonly precipitate low-temperature minerals at and below the seabed, such as iron and manganese oxides and silica. The focused-flow (high temperature) and diffuse-flow (low temperature) systems support different biological communities.

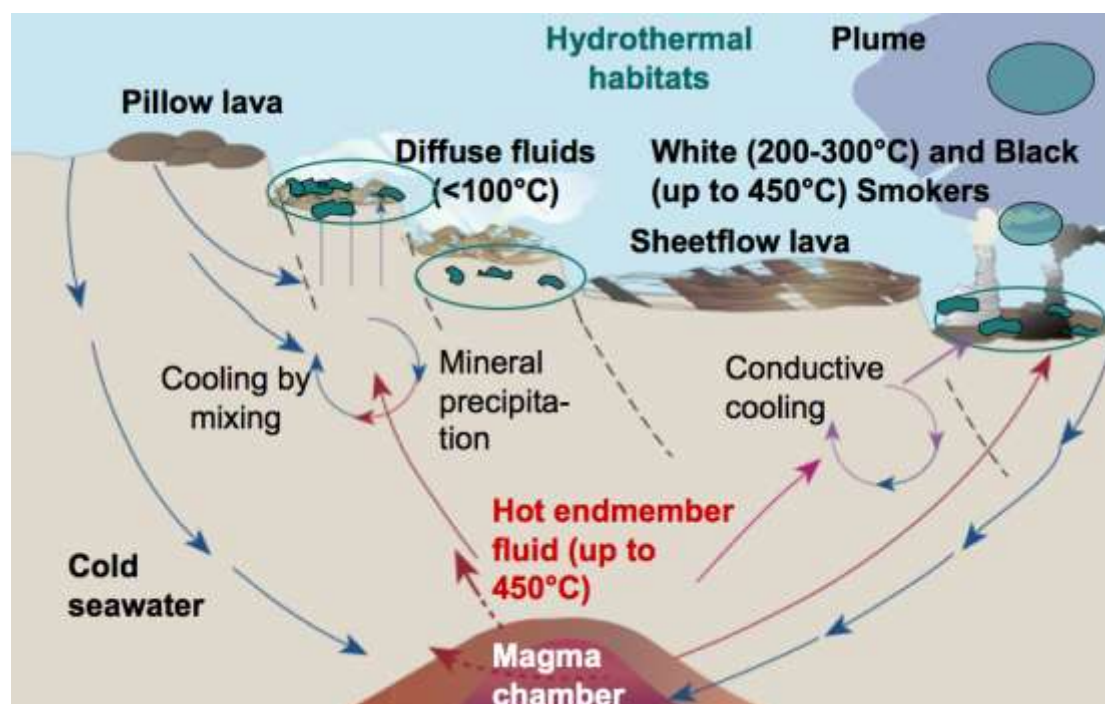


Figure 2: Components of a hydrothermal circulation cell and mineral deposits formed (model produced by Andrea Koschinsky, Jacobs University, Bremen, Germany).

Whether hydrothermal deposits are composed predominantly of iron sulphides and therefore of no economic interest, or contain high contents of copper, zinc, gold, and/or silver depends on a wide-variety of variables within the hydrothermal circulation cell. The dominant controls include the type of host rock that was leached, which can vary from ultramafic rocks to rhyolite to mixed-source sediments; the size and depth of the magma chamber; the temperature, redox state, and pH of the fluid; boiling and phase separate into vapor and brine—the temperature of boiling varies significantly with water depth; and magmatic contributions of volatiles and metals.

Comparison of oceanic spreading and volcanic arc systems

Hydrothermal systems in subduction-related environments and at mid-ocean ridges are similar as mentioned above, but distinct characteristics of each system influence the mineralogy and chemical composition of the sulphide-sulphate deposits. The main distinct characteristics of arc systems is more felsic and silicic host-rock compositions, much greater input of magmatic volatiles and metals into the hydrothermal circulation cell, and variable but generally shallow-water depths of precipitation of minerals, less than 1200 metres. Because of the shallower water depths, fluid temperatures are generally lower and boiling and phase separation are generally more common than they are at oceanic spreading centers. These conditions may produce higher gold, silver, and copper, contents, and more barite in the arc system deposits.

Characteristic of Mediterranean and Pacific volcanic arc hydrothermal systems

In the West Pacific, the dominant arc systems are the Izu-Bonin-Mariana (IBM) arc north of the equator and the Tonga-Kermadec and small arc-back-arc microplates south of the equator (Fig. 3). In the Pacific, active hydrothermal systems and sulphide-sulphate deposits have been found within the craters and calderas of large arc volcanoes, but they are not common in that setting; for example only one such deposit is known to occur along the 1200 km-long Mariana arc, in East Diamante caldera (Hein et al., 2013), as well as several craters and calderas in the Izu-Bonin and Kermadec arcs (e.g., de Ronde et al., 2011). Rather, most of the high-temperature vents and the largest sulphide deposits in the West Pacific occur at intraoceanic back-arc spreading centres such as the Lau Basin, North Fiji Basin, and Mariana Trough. Arc-related rifts in continental crust such as the Okinawa Trough have thick sediment cover and may be important sites of massive sulphide accumulation in the subsurface. These intraoceanic back-arc spreading centres and caldera-hosted deposits of the West Pacific are most analogous to the few hydrothermal deposits found thus far in the Mediterranean Sea arc systems.

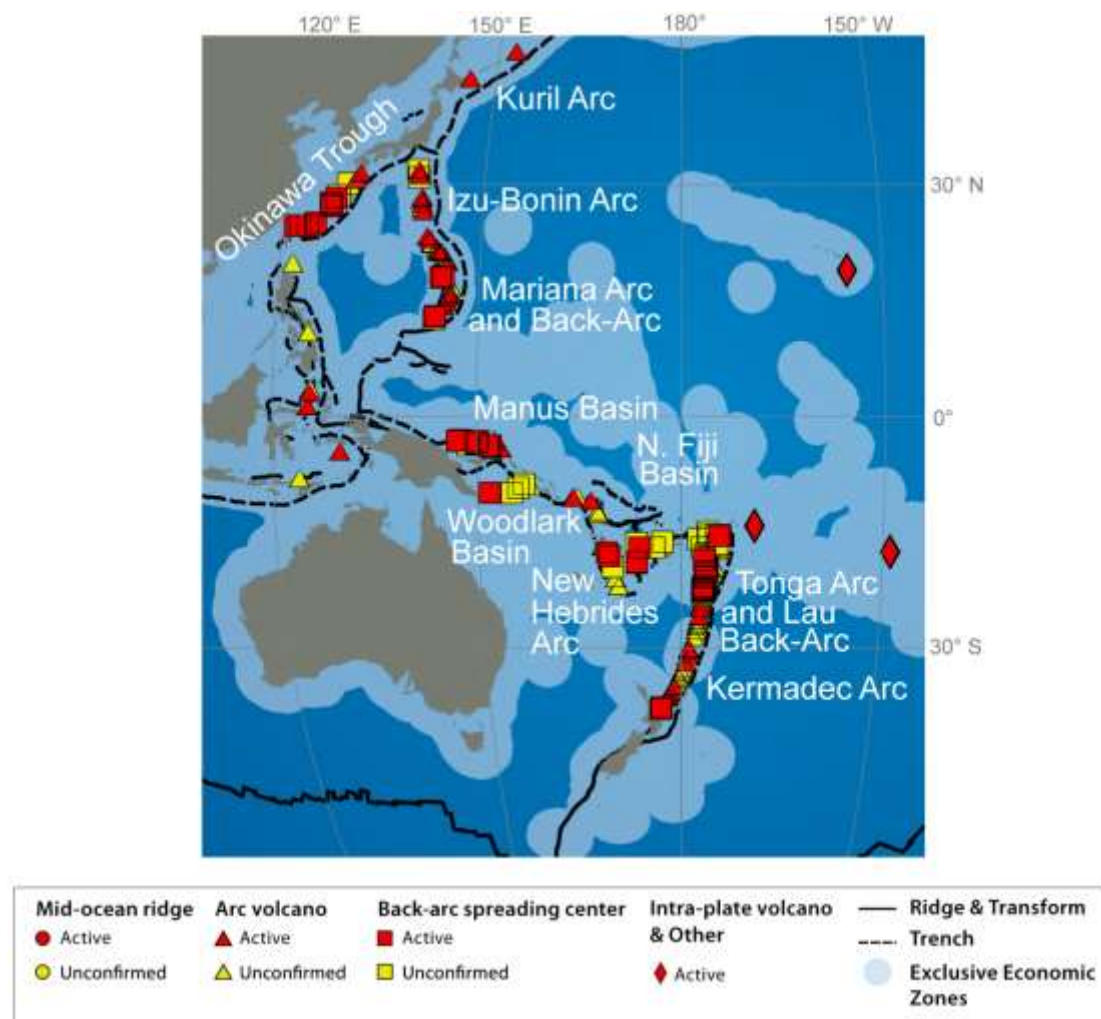


Figure 3: Map showing subduction system arcs and back-arc basins in the West Pacific (map modified from Beaulieu et al., 2010).

Most Mediterranean subduction-related hydrothermal systems and associated deposits are found in the Aeolian arc in the Tyrrhenian Sea and the Aegean Arc in the Aegean Sea (Fig. 4). In the Mediterranean arc systems, unlike the Pacific arc systems, most of the mineralization occurs on the islands or has been found hosted by sediment offshore in shallow water. In most of the volcanically active areas, hydrothermal deposits have probably formed below the seafloor at subbottom depths of tens of centimetres to tens of metres and are not exposed at the seafloor. The seafloor expression of the hydrothermal systems in both of these Mediterranean arcs is venting of warm fluids and especially gases, that produce iron, sulphur, and minor sulphide staining of surface sediment at the vent sites, as well as white bacterial mats, all of which are part of the low-temperature distal end of the hydrothermal systems (e.g. Cronan and Varnavas, 1999; Price et al., 2012; Stüben and Glasby, 1999). Less commonly, iron oxide crusts and silica and sulphur mounds also occur, as well as grains and small fragments of sulphides, the latter of which have been found in mud at and near the seafloor in the Aeolian arc (Savelli et al., 1999).

Hydrothermal-epithermal deposits on islands in the Aegean Arc may have formed from contributions of elements from seawater, magmatic fluid, and meteoric water systems (Alfieri et al., 2013; Naden et al., 2005). The best-known hydrothermal-epithermal deposits along the Aegean Arc occur on Milos Island and consist of gold and silver deposits at Proitis

Lias-Chondro Vouno; lead, zinc, and silver at Tridades-Galana-Agathia-Kondaros, and lead, zinc, silver, and manganese at Katsimoutis-Kondaros-Vani (Alfieris et al., 2013). Manganese was mined at Cape Vani from 1886-1909 and again from 1916-1928 (Liakopoulos et al., 2001); sulfur was mined from ancient times off and on and from 1862 until 1958, and hydrothermal barite from 1932 until recent times. Epithermal gold was discovered only recently, 1994, at Profitis Lias-Chondro Vouno (Plimer, 2000) and may be exploited in the future.

(A)



(B)

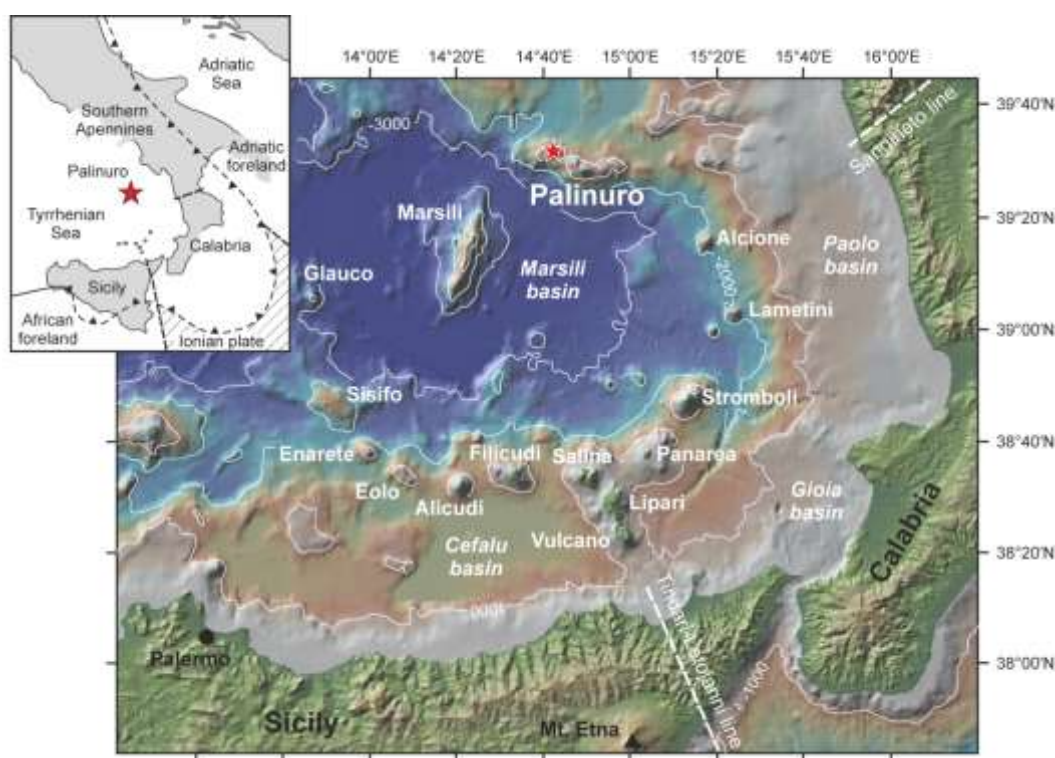


Figure 4: Maps showing subduction system arcs and back-arc basins in the Mediterranean (A) Aegean Arc (B) Aeolian Arc (from Petersen et al., 2013)

A comparison of the Vani manganese deposit on Milos Island with deposits from Enarete and Palinuro Seamounts in the Tyrrhenian Sea and Pacific Mariana Arc hydrothermal manganese shows many similarities. The iron (Fe)-manganese (Mn)-(cobalt (Co)+nickel (Ni)+copper (Cu))x10 ternary diagram shows that most of the Mariana Arc samples (Hein et al., 2008), as well as all of the Tyrrhenian Sea (Eckhardt et al., 1997) and Milos Island (Hein et al., 2000) samples plot within the hydrothermal field (Figure 5A). The subgroup of the Mariana Arc samples with greater than 26% manganese and the Milos Island samples all plot within the manganese end-member part of the hydrothermal field, while the Tyrrhenian Sea and Mariana samples with <21% manganese span nearly the entire hydrothermal iron-manganese hydrothermal field; three samples from the Mariana Arc plot within the hydrogenetic-hydrothermal transition zone and one sample plots within the hydrogenetic field because of unusually high cobalt and nickel contents compared to other hydrothermal manganese deposits (Hein et al., 2008)—these three samples are purely hydrothermal without a hydrogenetic component. Most arc-system hydrothermal manganese deposits can be modeled using a three-component system with aluminosilicate, manganese oxide, and iron oxide end-members. This relationship is shown on a Fe-Mn-silica (Si)x2 ternary plot, where most data plot along a line connecting the pure manganese end-member to a mean arc volcanic rock end-member (Fig. 5B). Data that do not fall along that line have a relatively greater Fe component and identify samples with a hydrothermal iron component, which is prominent for many Mariana and Tyrrhenian Sea samples, but not the Milos samples; iron is about equally distributed between the aluminosilicate and hydrothermal iron end-members in the Mariana samples (Hein et al., 2008). A ternary plot of molybdenum (Mo)-Ni + chromium (Cr)-Cu+zinc (Zn) was designed to identify the possible source rocks

that were leached of metals that were supplied to these hydrothermal manganese deposits (Figure 5C, Hein et al., 2008). The Milos Island samples plot near the Cu+Zn apex, which indicates a strong contribution from either the leaching of sulphides deposited at depth or non-deposition of sulphides at depth; Cu and Zn are usually sequestered by precipitation of sphalerite and chalcopyrite deeper in the hydrothermal system than where hydrothermal iron and Mn oxides form. The Mariana samples reflect a much more diverse set of source rocks leached in the hydrothermal systems along the length of the arc, with about an even distribution of samples with a sulfide source Cu+Zn, like the Milos samples, and a silicic-felsic (dacitic) source (Mo apex), reflecting high-temperature leaching of intermediate to acidic volcanic rocks. Unfortunately, Mo data were not included for the Tyrrhenian Sea samples, however Eckhardt et al. (1997) suggested that the metals in the hydrothermal manganese in this region was derived by adsorption from seawater. Ultramafic source rocks (Ni+Cr) are not a significant source for metals in the arc samples presented here.

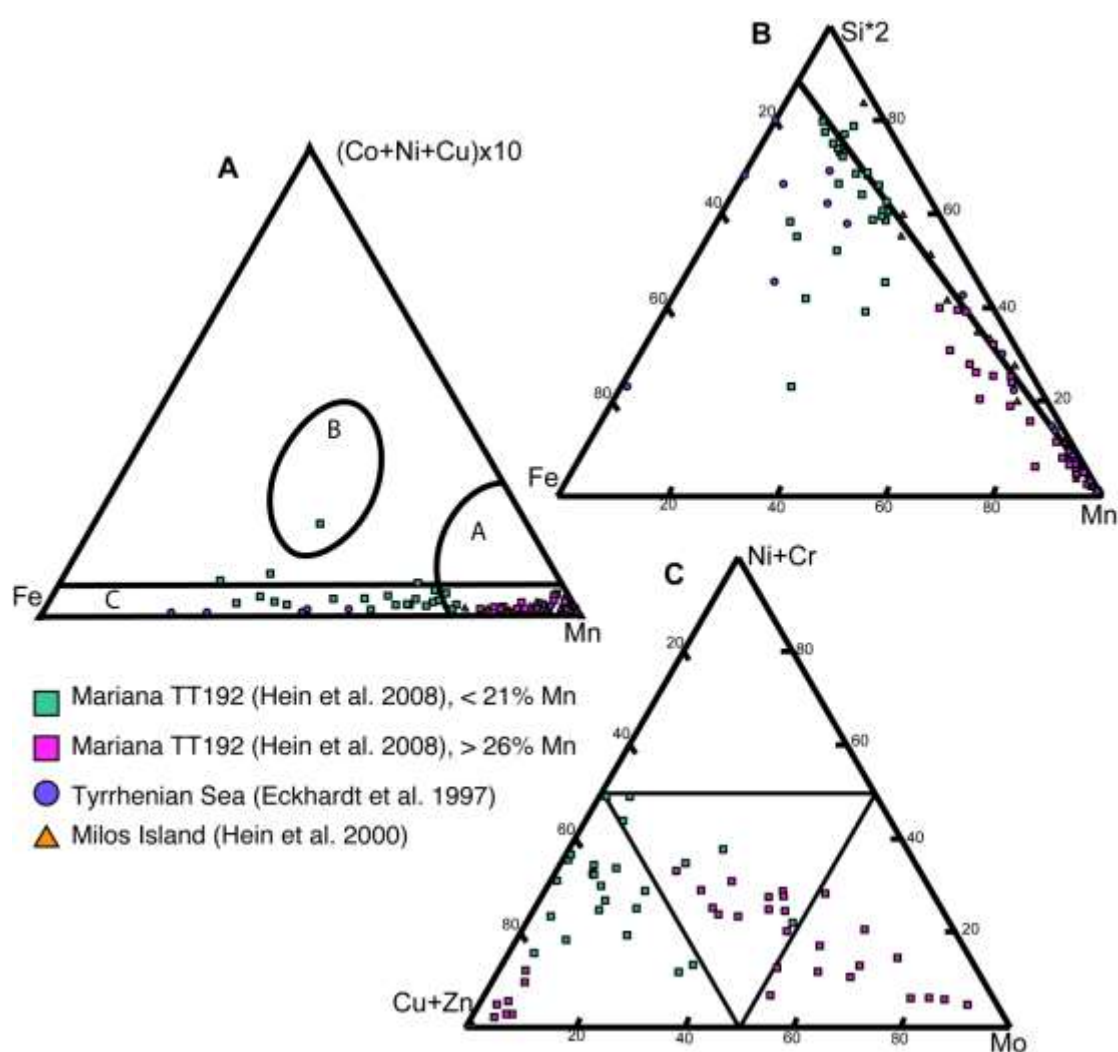


Figure 5: (A) Fe-Mn-(Co + Ni + Cu)x10 ternary diagram for hydrothermal manganese deposits from the Mariana volcanic arc (Hein et al., 2008); Milos Island, Aegean Arc (Hein et al., 2000), and the Tyrrhenian Sea (Eckhardt et al., 1997); field A is diagenetic, field B hydrogenetic, field C hydrothermal; (B) Fe-Mn-(Si)x2 ternary diagram for same samples as in Figure 5A; a line is drawn through the highest Mn sample and the average arc volcanic rock; (C) Discriminant ternary plot showing possible sources of trace metals in hydrothermal Mn deposits: Ni + Cr, leaching of ultramafic end-member; Cu + Zn, leaching of sulfide end-member, or nondeposition of sulfides at depth; Mo, high-temperature leaching of intermediate to acidic volcanic arc rocks.

The Aeolian Arc polymetallic sulphides (Hannington et al., 2005; Petersen et al., 2013) show close compositional similarities with many West Pacific arc sulphides (Hannington et al., 2005; Hein et al., 2013). Data for a Mariana Arc hydrothermal mound deposit discovered in 2009 on the flank of a resurgent dacite dome in East Diamante Caldera (Hein et al., 2013) plot very close on a ternary plot of Cu-Zn-lead(Pb)x10 to data for Aeolian Arc samples (Fig. 6); also, the Mariana Trough (back-arc basin), Palinuro Seamount, and Panarea Seamount data (Hannington et al., 2005) cluster with the mean data for drill-core sulphide samples from Palinuro Seamount (Petersen et al., 2013). These characteristics indicate that these two volcanic arc hydrothermal systems leach similar source rocks at similar temperatures accompanied by boiling, phase separation, and input of magmatic fluids.

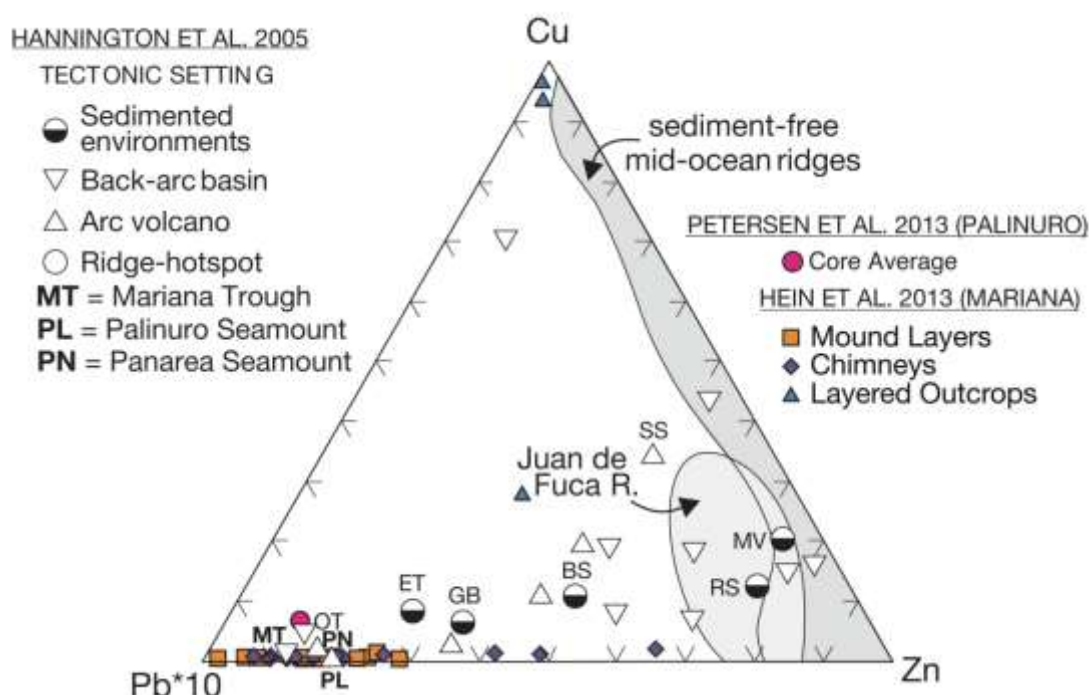


Figure 6: Cu-Zn-Pb_{x10} ternary plot showing the average bulk compositions of polymetallic sulfide deposits in different volcanic and tectonic settings; identified deposits are: AX = Axial Seamount, Juan de Fuca Ridge; BS = Bransfield Strait; ET = Escanaba trough; GB = Guaymas basin; LS = Lucky Strike, Mid-Atlantic Ridge; MT = Mariana trough, Alice Springs; MV = Middle Valley; OT = Okinawa trough, JADE site; PL = Palinuro Seamount; PN = Panarea Seamount; RS = Atlantis II Deep, Red Sea; SS = Suiyo Seamount, Izu-Bonin arc (From Hannington et al., 2005 with data added from Hein et al., 2013 and Petersen et al., 2013).

Future studies in the Aegean Arc

The paucity of seafloor hydrothermal sulphide-sulphate deposits is apparently characteristic of the Aeolian and Aegean arcs. However, offshore research/exploration programs for hydrothermal mineral deposits along the Aegean Arc are very few and seafloor sulphide-sulphate deposits may yet be found. A water-column survey looking for tracers of hydrothermal activity was carried out recently in the Aeolian Arc, and six out of 10 submarine volcanoes surveyed showed evidence of hydrothermal venting (Lupton et al., 2011). The strongest signal came from a water depth of 610 metres around Marsili seamount. A similar comprehensive water-column survey needs to be carried out along the Aegean Arc.

Recent shallow drilling in the Aeolian arc has confirmed that hydrothermal sulphide-sulphate deposits do occur below the seafloor, at centimetres to many metres depth—in

fact a 4.85 metre-thick seafloor section of massive sulphides-sulphates was recovered at one location at 612 metres water depth (Petersen et al., 2013). Because of the high sedimentation rates in the Aegean and Tyrrhenian Seas, it is likely that most hydrothermal deposits will have developed below the seafloor and this offers a challenging opportunity for exploration geologists. If true, this is significant, because sediment overlying hydrothermal systems acts as a reservoir for the accumulation of metals and as a thermal blanket to keep temperatures high, so resultant metal deposits can be large compared to seafloor deposits and enriched in metals of economic interest.

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